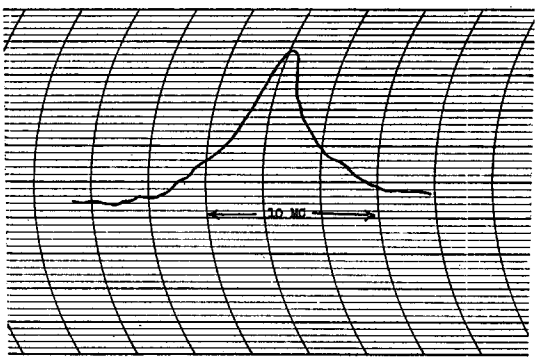

FIG. 1. $J=6-7$; absorption of $CHCl_3$[35].

parameters as:

$$d_{C-Cl}=1.761\mp0.004\text{A} \qquad d_{Cl-Cl}=2.908\mp0.004\text{A}$$
$$\angle H-C-Cl=108°\,0'\mp40' \qquad \angle Cl-C-Cl=112°-0'\mp40'.$$

The C—Cl bond is shorter than the value[5] of 1.783A found for methyl chloride and is, within experimental error, equal to the value of 1.760±0.005A found by electron diffraction[7] for CCl_4. The data also agrees with the somewhat less precise electron diffraction data on chloroform[8] and with Pauling's value of 1.76 for the sum of the single bond radii of carbon and chlorine.[9]

Further investigations with C^{13} enriched chloroform are planned to determine completely the structure as preliminary investigations show that the structure is insensitive to variations in the chlorine mass.

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The Planarity of the Urea Molecule*

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ARGUMENTS based on infra-red observations were recently presented by W. E. Keller for the planarity of the urea molecule in the crystalline state.[1] Though plausible, we have not found these completely convincing since the statement that in a nonplanar model one of the A_1 hydrogen bending fundamentals should be essentially inactive is based on certain assumptions, and not on a selection rule required by symmetry. The really conclusive evidence is to be found in the 3μ region where the resolving power of the spectrometer employed by Keller seems to have been inadequate. In the planar model four N–H valence frequencies may be active, two of which have the character A_1. In the nonplanar C_{2v} model only three of these fundamentals can be active, and only one of these has the character A_1.

Excellent absorption spectra with very high resolution were recently obtained in this laboratory, using polarized radiation and single micro crystals of urea. These observations were made possible by a reflecting microscope or "microilluminator," with polarizing attachment, designed especially to match the optical systems of both the Beckman IR-2 spectrometer and our large vacuum grating instrument.[2] The latter instrument, with lead sulfide detector cooled by solid CO_2, was used in the work mentioned.

As may be seen in Fig. 1, two pairs of intense bands were observed in the 2.9μ region, accompanied by much weaker bands on the long wave side, which are presumably combination frequencies or overtones. These pairs are incompletely resolved in ordinary light but with polarized radiation each was very definitely

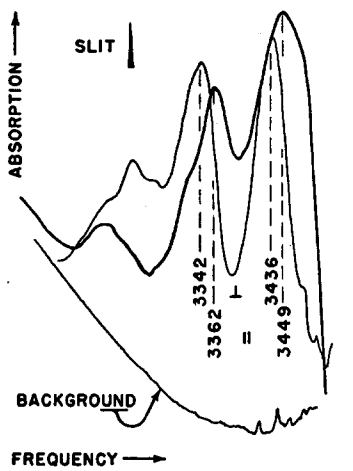

FIG. 1. Recorder tracings of the spectrum of a single urea crystal in polarized infra-red at 2.9μ, obtained with reflecting microscope and vacuum grating spectrometer. Frequencies of the four intense maxima are given. Symbols ⊥ and ∥ indicate direction of electric vector with respect to the tetragonal axis.

shown to consist of two components, one polarized perpendicular, and one parallel to the tetragonal axis. Because of their high intensity we regard it as very probable that the four strong bands are NH stretching fundamentals, and consider that the complete planarity of the urea molecule in the crystal is now reasonably well established by spectroscopic evidence.

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Eclipsed Configuration of the Hydrazine Molecule in the Solid State[1]

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THE configuration of the hydrogen atoms in the hydrazine molecule has been discussed for some time. Although the spectroscopic data have been interpreted on the basis of the staggered configuration of C_2 symmetry, they are apparently not in serious conflict with the *cis*-configuration, which is the eclipsed form of C_{2v} symmetry[3] (Fig. 1). The observed dipole moment[4,5] of 1.90 debyes suggests an angle φ, between the projected bisectors of the HNH bonds, of about 84°. Because of the nature of this argument, this value might well be ±20° or more. These dipole moment results are supported by the theoretical considerations of Penny and Sutherland[6] who find φ to be about 90°, or slightly greater. From the nature of hydrogen bonding in hydrazinium difluoride[7] and in hydrazinium dichloride[8] it is inferred that the